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COMPLETE SPECIFICATION

Process for Refining Raw Lactam

We, TOYO RAYON KABUSHIKI KAISHA, a Japanese body corporate of No. 2, 2-chome, Nihonbashi-Muromachi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for refining raw lactam, and more particularly to a process for refining raw lactam produced by subjecting cycloalkanoneoxime which is obtained by photonitrosation of cycloalkane to the Beckmann's reaction.

Heretofore, there has been proposed a process for refining raw lactam in which the aqueous solution of the raw lactam is treated with an anion exchange agent or a cation exchange agent, while patent specification No. 778751 describes a process in which the aqueous solution of the raw lactam having a concentration of 15 to 30 weight % is subjected to hydrogenation treatment at a temperature within the range, for example, of 85 to 100°C, after treatment with an ion exchange agent. These refining processes may be applicable to the refining of, for example, a raw lactam produced by means of the phenol process to a satisfactory extent, but application of these processes to the raw lactam produced by subjecting to the Beckmann's rearrangement a cycloalkanoneoxime which has been obtained by photonitrosation of cycloalkane does not bring about sufficiently satisfactory refining effect. This is probably because the raw lactams obtained by the latter method have organic foreign materials difficult to remove by distillation and have insufficient ionization characteristics, such as chlorine substitution, or unsaturation, on account of which the raw lactam cannot be expected to be refined satisfactorily even by subjecting it to an ion exchange treatment directly or by subjecting it to the conventional hydrogenation treatment.

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In view of the above, one of the objects of the invention is to provide an improved process for refining raw lactam produced by subjecting cycloalkanoneoxime which is obtained by photonitrosation of cycloalkane to the Beckmann's reaction.

It has been discovered that lactam of sufficiently high quality may be obtained at a high efficiency by treating raw lactam with alkalis in a liquid phase, the lactam being produced by subjecting cycloalkanoneoxime obtained by photonitrosation of cycloalkane to the Beckmann's reaction, and subsequently hydrogenating it in the presence of a hydrogenating catalyst.

The method of preparing the starting raw lactam to be refined by the process of the invention has been known heretofore. When cycloalkane having 5 to 14 carbon atoms, preferably having 5 to 8 carbon atoms, is subjected to nitrosation with the use of such nitrosation agent as nitrosyl chloride, mixture of nitrogen oxide and chlorine gases, mixture of nitrosegas (mixture of NO and NO₂ gases) and hydrogen chloride, mixture of nitrosyl chloride and hydrogen chloride gases or mixture of nitrogen oxide and chlorine gases, a corresponding hydrochloride of cycloalkanoneoxime is obtained in an oily condition. The hydrochloride of cycloalkanoneoxime so obtained or cycloalkanoneoxime produced therefrom is then subjected to the Beckmann's reaction with the use of such catalysts as sulfuric acid and/or oleum to obtain the starting raw lactam. The raw lactam thus obtained is normally in the form of at least 50 weight % aqueous solution. The process for preparing the starting raw lactam itself is not the subject matter of the invention.

The process of the invention is characterized by treating the aforementioned raw lactam with alkalis in the liquid phase and simultaneously or subsequently subjecting it to catalytic hydrogenation.

Those alkalis employed in the invention in-

clude caustic soda or other alkali metal hydroxides such as caustic potash or alkali metal carbonates such as potassium carbonate. Such alkali is used in the amount of 0.1 to 5 weight percent depending on the weight of the raw lactam. The treating temperature is from 40 to 150°C while the treating period is from 0 to 5 hours. The treating period of 0 signifies that the alkali treatment and the hydrogenation treatment may be carried out simultaneously. In most cases, however, the alkali treatment is desirably performed first for about 30 minutes followed by the hydrogenation treatment.

As the solvents for the raw lactam used in the alkali treatment and/or hydrogenation treatment, organic solvents such as alcohol and benzene may be used but water is used preferably and advantageously. The concentration of lactam in the lactam solution to be treated is desired to be as high as possible (at least higher than about 50 weight %) in order to minimize a loss of the lactam through hydrolysis. In the instance of ϵ -caprolactam or ϵ -capryllactam, a concentration of at least about 70 weight % is recommendable.

Those hydrogenating catalysts employed in the hydrogenation treatment of the invention include normal hydrogenating catalysts having, for example, nickel, cobalt, platinum or palladium as the base.

The hydrogenation treatment is preferably carried out under heated and pressurized condition in order to accelerate hydrogen absorption though it may be performed at atmospheric temperature and pressure. An optimum combination of conditions may be determined dependent on the quality of the raw lactam and the kinds of catalysts but a temperature below 150°C, and preferably from 40 to 80°C, and a pressure below 50 atmospheres are normally employed.

In a preferable form of the invention, a raw lactam is treated with alkali in the liquid phase followed by the hydrogenation treatment thereof, and thereafter treated with ion exchange agents. Those ion exchange agents suitably used in the process of the invention include anion exchange resins having an amino group or a quaternary ammonium group and cation exchange resins having a carboxyl group or a sulfone group. These ion exchangers may be of free type or of salt type. The solution to be treated may be subjected to treatment with the anion exchange agent and with the cation exchange agent alternatively but the cation exchange treatment alone may be sufficient in some instances. In other instances, the solution may be treated with a mixture of anion and cation

exchange agents or with an amphoteric ion exchange agent.

The solution flow temperature should be above the room temperature and preferably above 40°C but below the yielding temperature of the ion exchange resin (normally from 100 to 120°C).

According to the present invention, nitrogen compounds hard to remove are transformed into ionic substances such as amines through the combined treatment of the alkali treatment and the hydrogenation treatment, which are removed effectively in the following treatment with the ion exchange agents.

Though the amount of such nitrogen compounds is normally less than 1/10 of the chlorolactam (contained as foreign material), the presence thereof in what small amount it may be will adversely affect the quality of lactam to a great extent. While such nitrogen compounds cannot be separated completely by distillation, these compounds may be removed to the allowable extent by means of the process of the invention.

By practising the invention, it will be possible to markedly reduce the volatile base content of the lactam, to improve the transmittance of the lactam aqueous solution in the ultraviolet zone and to noticeably improve the permanganic acid value, and the polymer (nylon) which is obtained by polymerizing ϵ -caprolactam refined according to the invention is outstandingly superior in colour and heat resistance and light resistance properties.

According to the invention in which hydrogenation is performed after or concurrently with the alkali treatment the resultant product is several times as superior in the life as that of the products of the conventional catalytic hydrogenation processes wherein no alkali treatment is conducted, when using the same hydrogenation catalyst.

EXAMPLE 1

500 g of 80% aqueous solution of raw ϵ -caprolactam were placed in a 1l reaction vessel, to which 10 g of 20% caustic soda and 1 g of palladium-carbon (containing 5% palladium) was added and hydrogen was added and hydrogen was introduced therein at a temperature of 50°C and under 5 atmospheres. After shaking for 2 hours, the reaction solution was taken out and subjected to vacuum distillation after having the catalyst filtered, whereby 390 g of pure white ϵ -caprolactam were obtained (which correspond to 97.5% of the raw lactam) having the following properties.

Melting point:	69°C
APHA:	5 (80% aqueous solution)
Permanganic acid value:	1800 seconds
Viscosity ratio of polymer:	250 (lg/100 cc 98% sulfuric acid)

In the instance of adding no caustic soda, the amount of the distillate lactam was only 378 g (which correspond to 94.5% of the raw lactam).

5 EXAMPLE 2

350 g raw ϵ -caprolactam was added to 75 g of 20% caustic potash aqueous solution and was heated at 120°C for 1 hour under a reduced pressure while distilling off water. After adding 2 g Ranay nickel, the solution was subjected to hydrogenation at 70°C for 1 hour under atmospheric pressure. Subsequently the catalyst was heat filtered and the solution vacuum distilled, thereby yielding 340 g refined lactam (which correspond to 97.2% of the raw lactam).

EXAMPLE 3

500 g aqueous solution of 50% raw capryllactam were added to 25 g sodium carbonate and 1.5 g of Ranay nickel were heated at 80°C for 2 hours after introducing hydrogen pressurized at 5 atmospheres. After distillation thereof, 240 g pure white ϵ -capryllactam (melting point: 73°C) were obtained (which correspond to 96.0% of the raw lactam).

EXAMPLE 4

200 g raw lauryl-lactam were dissolved in 300 g of 80% alcohol, to which were added 2 g caustic soda and 1 g Ranay nickel, and the solution thus obtained was treated with hydrogen at 120°C for 2.5 hours under 30 atmospheres. After vacuum distillation (75°C/3 mm Hg), 190 g pure white lauryl-lactam were obtained (which correspond to 95.0% of the raw lactam).

EXAMPLE 5

A.

20% caustic soda aqueous solution were added to 500 g of 80 weight % raw ϵ -capro-

lactam and after heating the mixture for 1 hour at 120°C while agitating thereof, 2 g nickel catalyst were added. The solution was then placed in a pressure container and, after introduction of hydrogen, was shaken for 3 hours at 70°C and at 3 kg/cm² pressure. After the treatment, the catalyst was filtered and then the solution was processed through a column provided with jackets of ion exchange resin Amberlite IRA 400 and Amberlite IR 200 ("Aberlite" is a Registered Trade Mark) while maintaining the solution temperature at 60°C, which was followed by vacuum concentration and distillation of the solution. 392 g pure white ϵ -caprolactam were yielded.

Comparative Example, Control B

Separately from the above, 2 g nickel catalyst were added to 500 g aqueous solution of 30 weight % raw ϵ -caprolactam, as in Example 5, which were shaken in a pressure container for 3 hours at 90°C under a pressure of 3 kg/cm after introducing hydrogen therein. After the treatment, the catalyst was removed by a filter and the solution was processed through a column provided with Amberlite IRA 400 and Amberlite IR 200. After vacuum concentration and distillation, 142 g ϵ -caprolactam were obtained.

Comparative Example, Control C

500 g aqueous solution of 50 weight % raw ϵ -caprolactam, same as of B above, were processed through a column provided with Amberlite IRA 400 and Amberlite IR 200, subsequent to which were vacuum concentrated and distilled. 236 g ϵ -caprolactam were obtained. The quality of ϵ -caprolactams obtained by the process of the invention (Refining Process A, Example 5), and by the process of Controls B and C was compared in the following.

Refining Process	Present Invention A	Control B	Control C
Yielding efficiency to raw lactam (%)	98.0	94.7	94.5
APHA of 80% aqueous solution (Hazen number)	5	20	40
Volatile bases (PPm as NH_3)	4	20	25
Transmittance (%) of 280 $\text{m}\mu$ (20% aqueous solution)	85.0	77.5	75.0
Permanganate value (sec)	2500	500	300
Heat resistance property in air, 130°C, 2 hours	Pure White	Light yellow	Yellow

EXAMPLE 6

To 572 g aqueous solution of 70 weight % raw ϵ -caprolactam was added 8 g potassium carbonate, which was agitated for 3 hours at 40°C. After adding 4 g nickel catalyst, the mixture was placed in a pressure reaction container and, after introduction of hydrogen pressurized at 50 kg/cm^2 into the container, was shaken for 2 hours at 150°C.

After the reaction, solid materials were removed by filtering and the solution was processed through a column provided with ion exchange resin Amberlite IRA 400 and IR 200 while maintaining the temperature at 80°C. 380 g ϵ -caprolactam were obtained after vacuum concentration and distillation. The ϵ -caprolactam thus obtained has 7 PPM volatile bases, 80.5% transmittance of 280 $\text{m}\mu$ and 2000 seconds permanganate value (PMV), showed little discoloration after 2 hours heating, remaining pure white.

EXAMPLE 7

A mixture of 500 g aqueous solution of 80 weight % raw ϵ -caprolactam, 2 g aqueous solution of caustic soda and 2 g palladium catalysts were charged in a pressure container, to which hydrogen at a pressure of 5 kg/cm^2 was introduced and shaken for 3 hours at 40°C. After separating the catalyst, the solution was processed through a column provided with ion exchange resin Amberlite. IRA 400 and IR 200 and thereafter vacuum concentrated and distilled. 388 g ϵ -caprolactam having 5 PPM volatile bases, 83.2% transmittance of 280 $\text{m}\mu$ and 2600 seconds PMV were obtained.

EXAMPLE 8

500 g aqueous solution of 50 weight % raw ϵ -caprolactam obtained by photonitrosation of cyclooctane were added to 2.5 g aqueous solution of 20% caustic potash and

0.5 g platinum catalyst. The mixture was shaken in a pressure container for 2 hours at 100°C after introducing hydrogen pressurized at 10 kg/cm^2 . The catalyst was removed and thereafter the solution was processed through a column provided with a combination of the ion exchange resin as in the preceding examples. After vacuum concentration and distillation, 240 g pure white ϵ -caprolactam having a melting point of 73°C were obtained (the yield ratio to the raw lactam was 96.0%).

EXAMPLE 9

200 g raw laurin lactam obtained by photonitrosation of cyclododecane were dissolved in 200 g ethyl alcohol, to which was added 1 g caustic potash and refluxed for 5 hours. The reduced substance was filtered, added to 2 g of 5% palladium carbon and shaken in a pressure container for 5 hours at 50°C after introducing hydrogen pressurized at 2 kg/cm^2 . Then, after removal of the catalyst, the solution was processed through a column provided with ion exchange resin Amberlites, IRA 400 and IR 200 while maintaining the temperature at 60°C. When ethyl alcohol was removed by distillation and laurin lactam was distilled at 175°C/3 mm Hg, 186 g pure white laurin lactam (yield ratio to the raw lactam was 93%) were obtained.

The expression "permanganate value" used herein means the time in seconds required by a solution of 1 g lactam in 100 ml twice-distilled water to decolorize, after addition thereto of 1 ml N/100 potassium permanganate, to the colour of a solution of 2g. copper sulphate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and 3g. cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 1000 ml. water.

The colour rating, expressed in APHA (=Hazen number) is the principal rating for assessing the purity of a lactam. A colour rating of 500 APHA corresponds to that of a solution of 1.25 g. potassium hexachloro-

platinate $KPtCl_6$ and 1g. cobalt $CoCl_2 \cdot 6H_2O$ in 100 ml. concentrated hydrochloric acid made up with 1 l. water. Lower colour ratings are obtained by appropriate dilution of this solution.

WHAT WE CLAIM IS:—

1. A process for refining raw lactam produced by subjecting to Beckmann's reaction a cycloalkanoneoxime which is obtained by photonitrosation of a cycloalkane, which comprises treating said raw lactam with an alkali in a liquid phase and subjecting it to hydrogenation treatment in the presence of a hydrogenation catalyst.
2. A process as claimed in claim 1, in which after hydrogenation the lactam is treated with an ion exchange agent.
3. A process as claimed in claim 2, in which a cation exchange agent is used as an ion exchange agent.
4. A process as claimed in claim 2 or 3, in which the ion exchange treatment is carried out at a temperature of at least $40^\circ C$.
5. A process as claimed in any preceding claim, in which at least one alkali selected from sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate is used in the quantity of about 0.1 to 5.0 weight % based on said raw lactam.
6. A process as claimed in claim 5 for refining raw lactam produced by subjecting Beckmann's reaction to a cycloalkanoneoxime which is obtained by photonitrosation of a cycloalkane having 5 to 14 carbon atoms, in which said raw lactam is treated with at least one alkali selected from sodium hydroxide, sodium carbonate and potassium carbonate in the quantity of about 0.1 to 5.0 weight % based on said raw lactam in a liquid phase containing at least 50 weight % concentration, subjected to hydrogenation treatment in the presence of a hydrogenating catalyst and thereafter treated with an ion exchange resin at a temperature of at least $40^\circ C$.
7. A process according to claim 1, substantially as described herein.
8. A process for refining raw lactam, performed substantially as described in any of the non-comparative Examples.
9. A lactam which has been refined by the process of any of the preceding claims.

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Reference has been directed in pursuance of Section 9, Subsection (1) of the Patents Act, 1949, to Patent No. 1,002,424.